

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 21-03-2003		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE  Polynitrogen Chemistry, Preparation and Characterization of (N <sub>5</sub> ) SnF <sub>6</sub> , N <sub>5</sub> SnF <sub>5</sub> , and N <sub>5</sub> B(CF <sub>3</sub> ) <sub>4</sub>				5a. CONTRACT NUMBER F04611-99-C-0025	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) William W. Wilson, Ashwani Vij, Vandana Vij, Eduard Bernhardt, Karl O. Christie				5d. PROJECT NUMBER DARP	
				5e. TASK NUMBER A025	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  ERC, Inc. 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-TP-2003-073	
12. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT  <div style="text-align: right; border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;">BEST AVAILABLE COPY 20030805 151</div>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  A	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Sheila Benner
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-5963

BEST AVAILABLE COPY

FILE

MEMORANDUM FOR PRS (In-House Contractor Publication)

21 Mar 2003

FROM: PROI (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2003-073**  
William Wilson (ERC) et al., "Polynitrogen Chemistry. Preparation and Characterization of  $(N_5)_2SnF_6$ ,  
 $N_5SnF_5$ , and  $N_5B(CF_3)_4$ "

(Statement A)

Journal: Angewandte Chemie

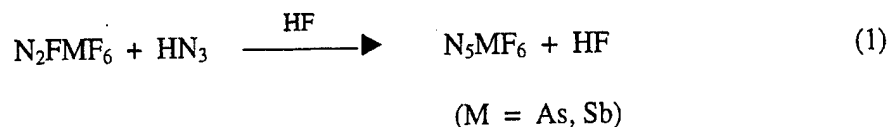
Carley  
55889

Y-0000000000

# Polynitrogen Chemistry. Preparation and Characterization of $(N_5)_2SnF_6$ , $N_5SnF_5$ , and $N_5B(CF_3)_4$ <sup>\*\*</sup>

William W. Wilson,<sup>\*</sup> Ashwani Vij, Vandana Vij, Eduard Bernhardt, and Karl O. Christe<sup>\*</sup>

During the past two decades, polynitrogen chemistry has received increasing attention.<sup>[1]</sup> While at the beginning, most of the efforts were devoted to theoretical studies, the recent syntheses of stable salts of the pentanitrogen(+1) cation,  $N_5^+$ ,<sup>[1,2]</sup> have given a strong impetus to experimental studies in this field. So far, the only method for generating  $N_5^+$  compounds has been their direct synthesis from  $N_2FAsF_6$  or  $N_2FSbF_6$  and  $HN_3$  in HF solution, according to Equation (1).



---

[\*] Dr W. W. Wilson, Dr. A. Vij, V. Vij, Prof. Dr. K. O. Christe  
ERC, Inc. and Space and Missile Propulsion Division,  
Air Force Research Laboratory (AFRL/PRSP)  
10 East Saturn Boulevard, Bldg 8451  
Edwards Air Force Base, CA 93524 (USA)  
Fax: (+1) 661-275-5471  
E-mail: [william.wilson@edwards.af.mil](mailto:william.wilson@edwards.af.mil); [karl.christe@edwards.af.mil](mailto:karl.christe@edwards.af.mil)  
and  
Loker Research Institute  
University of Southern California  
Los Angeles, CA 90089-1661 (USA)

Dr. E. Bernhardt  
FB 6-Anorganische Chemie  
Gerhard-Mercator-Universität Duisburg  
Lotharstrasse 1, 47048 Duisburg (Germany)

[\*\*] This work was funded by the Defense Advanced Research Projects Agency, with additional support from the Air Force Office of Scientific Research and the National Science Foundation. We thank Drs. R. Corley, A. Morrish, D. Woodbury, M. Berman, Prof. H. Willner, and M. Finze for their steady support, and Drs. R. Wagner, S. Schneider, T. Schroer, M. Gerken, and R. Haiges for their collaboration and stimulating discussions.

BEST AVAILABLE COPY

**DISTRIBUTION STATEMENT A**  
Approved for Public Release  
Distribution Unlimited

A major goal of this study was to increase the nitrogen content of the  $N_5^+$  salts by combining  $N_5^+$  with multiply charged anions. This presents a significant challenge because it results in structures with touching polynitrogen ions which will increase both the endothermicity and sensitivity of these compounds.

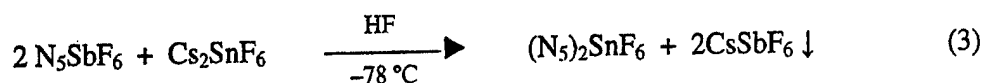
The general usefulness of the metathetical method is severely restricted by the small number of  $N_2F^+$  salts available. Except for reports on unstable  $N_2FBF_4^{[17]}$  and  $N_2FPF_6^{[18]}$  salts, no other  $N_2F^+$  compounds have been described in the literature. Therefore, it was desirable to develop a more general method for the syntheses of  $N_5^+$  salts, such as the exchange of  $SbF_6^-$  in  $N_5SbF_6$  for other anions. This situation resembles that previously encountered for the syntheses of  $NF_4^+$  salts.<sup>[19,20]</sup> Since  $SbF_5$  is among the strongest known Lewis acids,<sup>[21]</sup> displacement reactions are rarely feasible, and metathetical approaches are required.



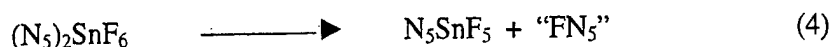
For a successful metathetical reaction, each ion must be compatible with the solvent, and both starting materials and one of the products must be highly soluble while the second reaction product must exhibit low solubility.

The choices of counter ions capable of forming stable  $N_5^+$  salts are limited. For room temperature stability, the strengths of the conjugate Lewis acids should exceed that of  $AsF_5$ , because  $N_5AsF_6$  is only marginally stable at room temperature.<sup>[11]</sup> The stability of the  $N_5^+$  salt might be further enhanced by the use of a weakly coordinating, bulky anion.

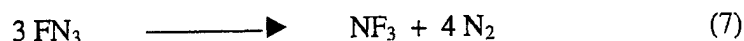
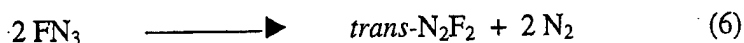
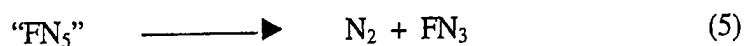
Several solvents were explored for conducting reaction (2). Anhydrous HF was found to be an excellent choice for the  $SnF_6^{2-}$  salt, as shown in Equation (3).



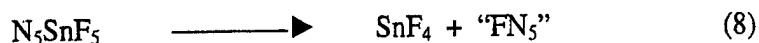
The resulting  $(N_5)_2SnF_6$  salt was obtained in high yield with a purity of about 94 wt %. The impurities were about 5 wt % of unreacted  $N_5^+SbF_6^-$  and 1 wt % of  $CsSbF_6$ . The  $(N_5)_2SnF_6$  salt is a white, friction sensitive (*Caution!*) solid, which is marginally stable at room temperature and decomposes at slightly higher temperature or on storage to  $N_5SnF_5$  with the loss of an "FN<sub>5</sub>" equivalent, as shown in Equation (4).



Because "FN<sub>5</sub>" is unstable with a predicted life time of nanoseconds,<sup>[22]</sup> only its primary decomposition products, FN<sub>3</sub> and N<sub>2</sub>, and secondary decomposition products, *trans*-N<sub>2</sub>F<sub>2</sub>, NF<sub>3</sub> and N<sub>2</sub>, were observed by checking for noncondensable gas at -196 °C and FT-IR spectroscopy. The relevant decomposition reactions are shown in Equations (5), (6), and (7).



The  $N_5SnF_5$  salt, formed by the controlled thermal decomposition of  $(N_5)_2SnF_6$ , is a white solid that starts to decompose at about 50 to 60 °C. The fact that the thermal stabilities of  $N_5SbF_6$ ,  $N_5[B(CF_3)_4]$  (see below), and  $N_5SnF_5$  are all comparable suggests that the thermal stability of the  $N_5^+$  cation is the limiting factor. The thermal decomposition of  $N_5SnF_5$  was studied by its material balance and vibrational spectroscopy and proceeds smoothly according to Equation (8), yielding  $SnF_4$  as the solid nonvolatile residue.



The  $(N_5)_2SnF_6$  and  $N_5SnF_5$  salts were characterized by vibrational (Tables 1 and 2, and Figure 1) and multinuclear NMR (Table 3 and Figure 2) spectroscopy. The Raman and infrared

spectra are in accord with the expectations for  $N_5^+$  and the fluorostannate anions.<sup>[1,2,23,24]</sup> One remarkable feature in the vibrational spectra of  $(N_5)_2SnF_6$  is the fact that the frequencies of all  $SnF_6^{2-}$  modes and of the  $N_5^+$  stretching modes are shifted to significantly higher frequencies, when compared to  $(NF_4)_2SnF_6$ <sup>[23]</sup> and the 1:1 salts of  $N_5^+$ .<sup>[1,2]</sup> In the absence of a crystal structure, we cannot provide a convincing explanation for this unexpected effect. It should also be noted that in mixtures of  $(N_5)_2SnF_6$  and  $N_5SnF_5$ , generated by partial decomposition of the former, only one set of bands with intermediate frequencies was observed and not two sets with the frequencies of the 2:1 and 1:1 salts. While the bands for  $SnF_6^{2-}$  are sharp and narrow, as expected for a monomeric octahedral anion, the bands due to  $SnF_5^-$  are broad and poorly defined. This is in accord with the results from the multinuclear NMR study which show  $SnF_5^-$  to be present as both a dimer and a cyclic tetramer.

The NMR spectra of  $N_5SnF_5$  in HF solution were recorded at  $-78^\circ C$ . The  $^{14}N$  spectrum showed a strong resonance at  $-164.7$  ppm and a very broad line at about  $-99.9$  ppm, characteristic for the  $N_\beta$  and the terminal  $N_\alpha$  atoms, respectively, of the  $N_5^+$  cation.<sup>[1]</sup> In addition to the signal due to HF (doublet at  $\delta = -189.8$  with  $^1J^{H-^{19}F} = 518.9$  Hz), the  $^{19}F$  spectrum showed two very similar sets of signals (Table 3) that varied somewhat in relative intensity from sample to sample and with temperature. The more intense set, having about twice the intensity of the weaker one, is assigned to the dimeric anion,  $Sn_2F_{10}^{2-}$ . The less intense set has the same area ratios and almost identical shifts and coupling constants, and therefore must belong to a species with an almost identical molecular structure. The only species that meets these requirements is the cyclic tetramer,  $Sn_4F_{20}^{4-}$ . Although the  $^{19}F$  NMR spectrum of  $Sn_2F_{10}^{2-}$  in  $SO_2$  solution has been reported previously,<sup>[25,26]</sup> its chemical shifts and coupling constants significantly deviate from those of the HF solution. This deviation is probably due to solvent

effects, as shown by recording the spectra of  $\text{Cs}_2\text{SnF}_6$  in HF solutions at  $-78$  (and  $23$ )  $^\circ\text{C}$ , respectively. They showed singlets at  $\delta = -160.5$  ( $-164.5$ ) ppm with  $|^1\text{J}^{19}\text{F}-^{119}\text{Sn}| = 1416$  ( $1437$ ) Hz and  $|^1\text{J}^{19}\text{F}-^{117}\text{Sn}| = 1355$  ( $1376$ ) Hz, deviating from the values,  $\delta = -139$  ppm and  $|^1\text{J}^{19}\text{F}-^{119}\text{Sn}| = 1604$  Hz,<sup>[25]</sup> reported for  $\text{SnF}_6^{2-}$  in  $\text{SO}_2$  solution, by about the same amount as found for the  $\text{Sn}_2\text{F}_{10}^{2-}$  signals.<sup>[25]</sup> The  $^{119}\text{Sn}$  spectrum was also recorded and consisted of a complex multiplet (Figure 2). The observed spectrum was successfully simulated assuming first order triplets of triplets of triplets for both  $\text{Sn}_2\text{F}_{10}^{2-}$  and  $\text{Sn}_4\text{F}_{20}^{4-}$ , using the coupling constants similar to those derived from the tin satellite peaks in the  $^{19}\text{F}$  spectra. The  $^{119}\text{Sn}$  chemical shifts of  $\text{Sn}_2\text{F}_{10}^{2-}$  and  $\text{Sn}_4\text{F}_{20}^{4-}$  are also almost identical (difference of only  $0.4$  ppm), thus confirming the close structural relationship of these two anions.

The synthesis of a stable  $(\text{N}_5)_2\text{SnF}_6$  salt is highly significant because it represents the first example of an  $\text{N}_5^+$  salt that contains two polynitrogen cations per anion. It demonstrates that *salts with touching polynitrogen cations can exist, and that the goal of an ionic nitrogen allotrope might be achievable.*

A particularly attractive counter-ion,  $\text{B}(\text{CF}_3)_4^-$ , was recently reported by Willner et al.<sup>[27]</sup> The Lewis acidity of its conjugate parent molecule  $\text{B}(\text{CF}_3)_3\text{CF}_2$  ( $\text{pF}^-$  value of  $11.77$ )<sup>[21]</sup> exceeds that of  $\text{SbF}_5$  ( $\text{pF}^-$  value of  $11.30$ ),<sup>[21]</sup> and its negative charge is distributed over 12 fluorine atoms, thus rendering it a weakly coordinating anion. For the  $\text{B}(\text{CF}_3)_4^-$  salts, HF was a poor solvent choice because the solubility differences between  $\text{MB}(\text{CF}_3)_4$  and  $\text{MSbF}_6$  ( $\text{M} = \text{alkali metal}$ ) were found to be too small for an effective metathesis. Although the  $\text{MB}(\text{CF}_3)_4$  salts are soluble in water, diethylether, tetrahydrofuran, acetonitrile, and acetone,<sup>[27]</sup> the incompatibility of  $\text{N}_5\text{SbF}_6$  with these solvents precluded their use. Therefore, the metathesis was carried out in  $\text{SO}_2$  solution, as shown in Equation (3).



The precipitate was filtered off and identified by vibrational spectroscopy as  $\text{KSbF}_6$ . The filtrate was taken to dryness and the residue was characterized by mass balance, and multinuclear NMR and vibrational spectroscopy as 83 wt %  $\text{N}_5\text{B}(\text{CF}_3)_4$  (Table 4), 14 wt % of  $\text{KSbF}_6$ , and 3 wt % of  $\text{N}_5\text{SbF}_6$ . The impurities are due to the fact that  $\text{KSbF}_6$  still has an appreciable solubility in  $\text{SO}_2$  even at  $-64^\circ\text{C}$ , and that a very small excess of  $\text{N}_5\text{SbF}_6$  was used in the reaction. Since the solubility of  $\text{CsSbF}_6$  in  $\text{SO}_2$  is lower than that of  $\text{KSbF}_6$ , the purity of  $\text{N}_5\text{B}(\text{CF}_3)_4$  could be further improved by using  $\text{CsB}(\text{CF}_3)_4$  in place of  $\text{KB}(\text{CF}_3)_4$  in the above described metathesis reaction. However, attempts to purify the crude product by recrystallization or to grow single crystals of  $\text{N}_5\text{B}(\text{CF}_3)_4$  from HF solution have so far been unsuccessful. They resulted in a reverse metathesis in which the  $\text{KSbF}_6$  impurity reacted with the  $\text{N}_5\text{B}(\text{CF}_3)_4$  producing  $\text{KB}(\text{CF}_3)_4$  and  $\text{N}_5\text{SbF}_6$ .

Multinuclear NMR spectra were recorded for  $\text{N}_5\text{B}(\text{CF}_3)_4$  in  $\text{SO}_2$  solution at room temperature. In the  $^{14}\text{N}$  spectrum, the  $\text{N}_\beta$  atom of  $\text{N}_5^+$  was observed at  $\delta = -163.9$  ppm, in accord with the value of  $-165.3$  ppm, reported previously for  $\text{N}_5\text{AsF}_6$  in HF solution at  $-63^\circ\text{C}$ .<sup>[11]</sup> In the  $^{11}\text{B}$  NMR spectrum, a 13 line resonance was observed at  $\delta = -18.0$  ppm with  $^2J(^{11}\text{B}-^{19}\text{F}) = 25.7$  Hz, in close agreement with the values previously reported for  $\text{KB}(\text{CF}_3)_4$  ( $\delta = -18.9$  ppm,  $^2J(^{11}\text{B}-^{19}\text{F}) = 25.9$  Hz) in  $\text{CD}_3\text{CN}$  solution.<sup>[27]</sup> In the  $^{13}\text{C}$  NMR spectrum, a quartet of quartets at  $\delta = 133.75$  ppm with  $^1J(^{13}\text{C}-^{19}\text{F}) = 301.8$  Hz and  $^1J(^{11}\text{B}-^{13}\text{C}) = 72.1$  Hz are in very good agreement with the previously reported values for  $\text{KB}(\text{CF}_3)_4$  ( $\delta = 132.9$  ppm,  $^1J(^{13}\text{C}-^{19}\text{F}) = 304.3$  Hz and  $^1J(^{11}\text{B}-^{13}\text{C}) = 73.4$  Hz).<sup>[27]</sup> There was no evidence for any decomposition products, nor any other unidentified species in the  $\text{SO}_2$  solution of  $\text{N}_5\text{B}(\text{CF}_3)_4$ .

The infrared and Raman spectra of solid  $\text{N}_5\text{B}(\text{CF}_3)_4$  were recorded and are summarized in Table 4. The observed frequencies and intensities are in good agreement with those previously



reported for  $N_5^+$  in  $N_5SbF_6$ <sup>[2]</sup> and  $N_5AsF_6$ <sup>[1]</sup> and for  $B(CF_3)_4^-$  in its alkali metal salts,<sup>[27]</sup> and establish that  $N_5B(CF_3)_4$  is the main product of the metathetical reaction of  $N_5SbF_6$  with  $KB(CF_3)_4$ .

The thermal stability of the  $N_5B(CF_3)_4$  was studied by DSC. In all runs, a moderately sized exothermic effect was always observed with an onset at 50 °C and with a maximum at ~66 °C. Additional exotherms were observed at ~93 °C and ~225 °C, but only the first exotherm is due to the decomposition of the  $N_5B(CF_3)_4$  salt. When the sample was heated to only 75 °C and then cooled back to room temperature before being reheated to 75 °C, the first exotherm was no longer observed, and the residue left in the Al pan no longer exhibited bands for  $N_5^+$  in the IR spectrum, but still showed bands for  $B(CF_3)_4^-$ . The thermal stability of  $N_5B(CF_3)_4$  is surprisingly high and approaches that of the  $N_5SbF_6$  salt (70 °C). It appears that the thermal stability of the  $N_5^+$  cation itself might be the limiting factor, and that the thermal decomposition of these salts is triggered by the decay of the  $N_5^+$  cation. The thermal stability of the  $B(CF_3)_4^-$  anion is high; even after being heated to 250 °C, the infrared bands due to the  $B(CF_3)_4^-$  anion persisted.

In summary,  $N_5SbF_6$  was successfully converted by metathesis into  $N_5B(CF_3)_4$  and  $(N_5)_2SnF_6$ . The latter salt is especially noteworthy because it contains two  $N_5^+$  cations per anion, thus demonstrating that salts with touching polynitrogen cations can be prepared. This constitutes an important milestone towards our ultimate goal of synthesizing a stable, ionic nitrogen allotrope. Although the  $(N_5)_2SnF_6$  salt is friction sensitive, its stepwise decomposition can be achieved, yielding  $N_5SnF_5$ . Multinuclear NMR spectra show that in HF solution the  $SnF_5^-$  anion exists as a mixture of  $Sn_2F_{10}^{2-}$  and  $Sn_4F_{20}^{4-}$  anions.

### *Experimental Section*

*Caution!  $N_5SbF_6$  is a highly energetic oxidizer. Contact with potential fuels must be avoided. This material should be handled on a small scale while using appropriate safety precautions such as face shields, leather gloves and protective clothing. The  $(N_5)_2SnF_6$  salt is friction sensitive and must be handled with special caution.*

The  $N_5SbF_6$  was prepared from  $N_2FSbF_6$  and  $HN_3$  in HF as previously described.<sup>[2]</sup> The  $KB(CF_3)_4$  was prepared from  $KB(CN)_4$  and  $ClF_3$  according to the literature method.<sup>[27]</sup> The  $Cs_2SnF_6$  was generated by reaction of a 2:1 mixture of  $CsF$  and  $SnF_2$  in 48% aqueous HF solution with a slight excess of 30% aqueous  $H_2O_2$  at 0 °C. The  $SO_2$  (anhydrous, >99.9%) was supplied by Air Products and was used as received. The HF was from Matheson and was dried by storage over  $BiF_3$  before use. Infrared spectra were recorded on a Mattson Galaxy 5030 FTIR spectrometer using neat powders that were sandwiched between two  $AgCl$  windows in a Barnes Engineering Co. mini-press. Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd-YAG laser at 1064 nm and neat powders in flamed out Pyrex glass capillaries sealed with Halocarbon wax. Multinuclear NMR spectra were recorded on a Bruker Avance 400 FT-NMR spectrometer using  $SO_2$  or HF solutions and 3 mm i.d. Teflon-FEP tubes (Wilma Glass Co.), heat-sealed and placed in 5 mm o.d. glass NMR tubes (Wilma Glass Co.). The thermal stabilities were determined on a DuPont Model 910 Differential Scanning Calorimeter using 0.5-1.8 mg samples in dry hermetically sealed aluminum pans and a heating rate of 10 °C/min. The data were analyzed with a DuPont Model 2000 Thermal Analyst.

The metathetical synthesis of  $N_5B(CF_3)_4$  was carried out using a stainless-steel-Teflon vacuum line<sup>[28]</sup> and a double Teflon-FEP U-tube apparatus that consisted of a reaction U-tube, a porous Teflon filter assembly, and a receiver U-tube.<sup>[23]</sup> The double U-tube was equipped with

two stainless-steel valves, and two Teflon-coated magnetic stirring bars, one in each of the two U-tubes.  $\text{N}_5\text{SbF}_6$  (1.053 mmol) was reacted with  $\text{KB}(\text{CF}_3)_4$  (1.013 mmol) in 1.8 mL of anhydrous  $\text{SO}_2$  in the reaction U-Tube at  $-64^\circ\text{C}$ . The reaction mixture was stirred at that temperature for one h to ensure complete reaction before cooling of the filter assembly to  $-78^\circ\text{C}$  with powdered dry ice. The mixture was filtered under 1.5 atm  $\text{N}_2$  pressure to remove the precipitated  $\text{KSbF}_6$  from the  $\text{SO}_2$  solution containing the  $\text{N}_5\text{B}(\text{CF}_3)_4$ . The  $\text{SO}_2$  was removed in vacuo at  $-64^\circ\text{C}$  leaving behind a white solid in the receiver U-tube. Based upon the observed mass balance and FT-IR and FT-Raman spectroscopy, the filter cake consisted of 0.2185 g  $\text{KSbF}_6$  (0.2783 g expected for 1.013 mmol) with only traces of  $\text{N}_5\text{B}(\text{CF}_3)_4$  from the mother liquor. The filtrate residue consisted of 0.4335 g of 83.37 wt%  $\text{N}_5\text{B}(\text{CF}_3)_4$ , 2.81 wt%  $\text{N}_5\text{SbF}_6$ , and 13.82 wt%  $\text{KSbF}_6$  (0.3615 g expected for 1.013 mmol  $\text{N}_5\text{B}(\text{CF}_3)_4$ , plus 0.0122 g expected for 0.0399 mmol of excess  $\text{N}_5\text{SbF}_6$ , and 0.0598 g expected for 0.2179 mmol  $\text{KSbF}_6$ ).

The synthesis of  $(\text{N}_5)_2\text{SnF}_6$  was carried out metathetically using the same type of double U-Tube as described above.  $\text{N}_5\text{SbF}_6$  (0.9430 g, 3.084 mmol) and  $\text{Cs}_2\text{SnF}_6$  (0.7513 g, 1.507 mmol) were added to the reaction U-Tube inside the drybox. HF was condensed into the reaction U-Tube at  $-196^\circ\text{C}$  on the vacuum line. The reaction mixture was warmed to  $-78^\circ\text{C}$  and stirred for about 10 minutes to reduce the possibility of localized heating of the reactants as they were initially solvated. Afterwards, the reaction mixture was allowed to slowly warm to room temperature with constant agitation over ~10 minutes; this was followed by constant stirring for another 30 minutes to ensure that the metathesis reaction has gone to completion. The reaction U-Tube was then cooled to  $-196^\circ\text{C}$  and checked for noncondensibles; none were found indicating that there was no decomposition of any  $\text{N}_5^+$  salt. The reaction mixture was

warmed to room temperature and stirred again for 15 minutes before the mixture was cooled to  $-78\text{ }^{\circ}\text{C}$  for 15 minutes in preparation for the low-temperature filtration procedure. At that point the filter assembly was cooled briefly to  $-78\text{ }^{\circ}\text{C}$  with powdered dry ice, and the mixture was filtered under 1.5 atm  $\text{N}_2$  pressure to remove the precipitated  $\text{CsSbF}_6$  from the  $(\text{N}_5)_2\text{SnF}_6/\text{HF}$  filtrate which was collected in the receiver U-Tube at  $-78\text{ }^{\circ}\text{C}$ . The gaseous  $\text{N}_2$  was evacuated from the double U-Tube, and the receiver U-Tube was warmed to  $-64\text{ }^{\circ}\text{C}$ . The HF was removed in vacuo at  $-64\text{ }^{\circ}\text{C}$  over several hours until only some clear colorless droplets were seen in the receiver U-Tube. The  $-64\text{ }^{\circ}\text{C}$  bath was removed with continued pumping on the reaction products as they gradually warmed to room temperature. Finally, the white solid  $(\text{N}_5)_2\text{SnF}_6$  product appeared in the receiver U-Tube after about 5 minutes; pumping was continued for one additional hour at room temperature to ensure the complete removal of the HF solvent. Based upon mass measurements, FT-IR and FT-Raman spectroscopy, the filter cake consisted of 1.2267 g of 90.1wt%  $\text{CsSbF}_6$ , and 9.9 wt%  $(\text{N}_5)_2\text{SnF}_6$  (1.1047 g expected for 2.997 mmol  $\text{CsSbF}_6$  and 0.1220 g expected for 0.327 mmol  $(\text{N}_5)_2\text{SnF}_6$ ). Using the same methods of investigation, the reaction products were found to consist of 0.4676 g of 94.0 wt%  $(\text{N}_5)_2\text{SnF}_6$ , 4.6 wt%  $\text{N}_5\text{SbF}_6$ , and 1.4 wt%  $\text{CsSbF}_6$  (0.4398 g expected for 1.180 mmol  $(\text{N}_5)_2\text{SnF}_6$ , plus 0.0213 g expected for 0.0697 mmol of excess  $\text{N}_5\text{SbF}_6$ , and 0.0065 g expected for 0.0176 mmol  $\text{CsSbF}_6$ ).

**Keywords:** fluorostannate anions · NMR spectroscopy · pentanitrogen(+1) cation · polynitrogen · tetrakis(trifluoromethyl)borate anion · vibrational spectroscopy

- 
- [1] K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112; *Angew. Chem. Int. Ed. Eng.* **1999**, *38*, 2004.

- [2] A. Vij, W. W. Wilson, V. Vij, F. S. Tham, J. A. Sheehy, K. O. Christe, *J. Am. Chem. Soc.* **2001**, *123*, 6308.
- [3] G. A. Olah, G. K. S. Prakash, G. Rasul, *J. Am. Chem. Soc.* **2001**, *123*, 3308.
- [4] M. T. Nguyen, T. K. Ha, *Chem. Phys. Lett.* **2001**, *335*, 311.
- [5] S. Fau, R. J. Bartlett, *J. Phys. Chem. A* **2001**, *105*, 4096.
- [6] R. J. Bartlett, *Chem. Ind.* **2000**, 140, and references cited therein; a compilation of data for N<sub>2</sub> to N<sub>10</sub> can be found at <http://www.qtb.ufl.edu/~bartlett/polynitrogen.pdf>.
- [7] G. Chung, M. W. Schmidt, M. S. Gordon, *J. Phys. Chem. A* **2000**, *104*, 5647, and references cited therein.
- [8] M. N. Glukhovtsev, H. Jiao, P. v. Rague Schleyer, *Inorg. Chem.* **1996**, *35*, 7124, and references cited therein.
- [9] H. H. Michels, J. A. Montgomery, Jr., K. O. Christe, D. A. Dixon, *J. Phys. Chem.* **1995**, *99*, 187.
- [10] G. Schatte, H. Willner, *Z. Naturforsch.* **1991**, *46 b*, 483.
- [11] G. Rasul, G. K. S. Prakash, G. A. Olah, *J. Am. Chem. Soc.* **1994**, *116*, 8985.
- [12] W. E. Thompson, M. E. Jacox, *J. Chem. Phys.* **1990**, *93*, 3856.
- [13] J. P. Zheng, J. Waluk, J. Spanget-Larsen, D. M. Blake, J. G. Radziszewski, *Chem. Phys. Lett.* **2000**, *328*, 227.
- [14] T. Ruchti, T. Speck, J. P. Connelly, E. J. Bieske, H. Linnartz, J. P. Maier, *J. Chem. Phys.* **1996**, *105*, 2591.
- [15] F. Cacace, G. de Petris, A. Troiani, *Science* **2002**, *295*, 480.
- [16] M. I. Eremets, R. J. Hemley, H. Mao, E. Gregoryanz, *Nature* **2001**, *411*, 170.
- [17] A. V. Pankratov, N. I. Savenkova, *Russ. J. Inorg. Chem.* **1968**, *13*, 1345.
- [18] K. O. Christe, R. D. Wilson, W. W. Wilson, R. Bau, S. Sukumar, D. A. Dixon, *J. Am. Chem. Soc.* **1991**, *113*, 3795.
- [19] a) K. O. Christe, J. P. Guertin, A. E. Pavlath, *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 83; b) W. W. Wilson, K. O. Christe, *J. Fluorine Chem.* **1980**, *15*, 83; c) K. O. Christe, W. W. Wilson, R. D. Wilson, *Inorg. Chem.* **1980**, *19*, 1494; d) K. O. Christe, W. W. Wilson, R. D. Wilson, *Inorg. Chem.* **1980**, *19*, 3254; e) W. W. Wilson, K. O. Christe, *J. Fluorine Chem.* **1982**, *19*, 253.
- [20] I. V. Nikikitin, V. Ya. Rosolovskii, *Russ. Chem. Rev.* **1985**, *54*, 426.

- [21] K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson J. A. Sheehy, J. A. Boatz, *J. Fluorine Chem.* **2000**, *101*, 151; K. O. Christe, D. A. Dixon, paper 53, presented at the 16<sup>th</sup> ACS Winter Fluorine Conference, St. Pete Beach, FL, Jan. 12-17, 2003.
- [22] H. M. Netzloff, M. S. Gordon, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, J. A. Boatz, *J. Chem. Phys.*, submitted for publication.
- [23] K. O. Christe, C. J. Schack, R. D. Wilson, *Inorg.Chem.* **1977**, *16*, 849.
- [24] K. O. Christe, C. J. Schack, *Inorg.Chem.* **1978**, *17*, 2749.
- [25] P. A. W. Dean, *Can. J. Chem.* **1973**, *51*, 4024.
- [26] P. A. W. Dean, D. F. Evans, *J. Chem. Soc. A* **1967**, 698.
- [27] E. Bernhardt, G. Henkel, H. Willner, G. Pawelke, H. Burger, *Chem. Eur. J.* **2001**, *7*, 4696.
- [28] K. O. Christe, R. D. Wilson, C. J. Schack, *Inorg. Synth.* **1986**, *24*, 3.

Table 1. Raman and Infrared spectra<sup>a</sup> of solid (N<sub>5</sub>)<sub>2</sub>SnF<sub>6</sub> and their assignments

Obsd frequencies, cm <sup>-1</sup> , and rel intens		Assignments (point group)	
Raman	Infrared	N <sub>5</sub> <sup>+</sup> (C <sub>2v</sub> )	SnF <sub>6</sub> <sup>2-</sup> (O <sub>h</sub> )
2287 (10.0) }	2288 m	v <sub>1</sub> (A <sub>1</sub> )	
2274 (1.9)			
2227 (1.9)	2228 s	v <sub>7</sub> (B <sub>2</sub> )	
2210 (0+)			
2170 (0.2)			
1112 (0+)	1112 s	v <sub>8</sub> (B <sub>2</sub> )	
	1083 m	(v <sub>3</sub> + v <sub>9</sub> )(B <sub>2</sub> ) = 1089	
881 (1.3)	881 w	v <sub>2</sub> (A <sub>1</sub> )	
822 (0.1)		2v <sub>9</sub> (A <sub>1</sub> ) = 834	
672 (2.6)		v <sub>3</sub> (A <sub>1</sub> )	
	611 vs		v <sub>3</sub> (F <sub>1u</sub> )
600 (6.1)	602 vw		v <sub>1</sub> (A <sub>1g</sub> )
508 (0.4)			v <sub>2</sub> (E <sub>g</sub> )
475 (0.2)		v <sub>5</sub> (A <sub>2</sub> )	
	417 ms	v <sub>6</sub> (B <sub>1</sub> )	
417 (0.5)		v <sub>9</sub> (B <sub>2</sub> )	
266 (1.2)			v <sub>5</sub> (F <sub>2g</sub> )
203 (3.0) }		v <sub>4</sub> (A <sub>1</sub> )	
195 (4.4)			
159 (1.0)			
126 (9.9) }			
119 (4.0) }			
80 (4.0)			
		lattice vibrations	

<sup>a</sup>The following bands due to the SbF<sub>6</sub><sup>-</sup> impurity were also observed. Ra: 654 (1.0), v<sub>1</sub>; 572 (0+), v<sub>2</sub>; 282 (0.3), v<sub>5</sub>.

Table 2. Raman and Infrared spectra<sup>a</sup> of solid  $\text{N}_5\text{SnF}_5$  and their assignments

Obsd frequencies, $\text{cm}^{-1}$ , and rel intens		Assignments (point group)	
Raman	Infrared	$\text{N}_5^+$ ( $\text{C}_{2v}$ )	$\text{SnF}_5^-$
2269 (10.0)	2270 m	$\nu_1(\text{A}_1)$	
2209 (2.0)	2212 s	$\nu_7(\text{B}_2)$	
	1230 w		comb. band
1090 (0+)	1094 ms	$\nu_8(\text{B}_2)$	
	1069 m	$(\nu_3 + \nu_9)(\text{B}_2) = 1090$	
	898 w		comb. band
875 (1.0)	878 vw	$\nu_2(\text{A}_1)$	
670 (1.8)		$\nu_3(\text{A}_1)$	
624 (3.8)	670 vs		
	610 s		
	590 sh		stretch. modes
475 (0.5), vbr	540 sh		
	519 m		
	421 m	$\nu_6(\text{B}_1)$	
420 (0.3)		$\nu_9(\text{B}_2)$	
260 sh, br			def. modes
202 (4.3)		$\nu_4(\text{A}_1)$	
120 (4)			lattice vibration

<sup>a</sup>The following bands due to the  $\text{SbF}_6^-$  impurity were also observed. Ra: 652 (1.0),  $\nu_1$ ; 575 (0+),  $\nu_2$ ; 280 (0.3),  $\nu_5$ .



Table 3. Multinuclear NMR spectra<sup>a</sup> of  $N_5SnF_5$ , recorded at  $-78^\circ\text{C}$  in HF solution

ion	atom	$\delta$ (multiplicity) (area ratio)	coupling constant (Hz)
$N_5^+$	$N_\beta$	-164.7 (s)	
	$N_\alpha$	-99.9br (s)	
$Sn_2F_{10}^{2-}$	$F_{eq}$	-173.0 (tr) (2)	$^2J^{19}F_{eq}-^{19}F_{ax} = 37.1$ ; $ ^1J^{19}F_{eq}-^{117}Sn  = 1671$ ; $ ^1J^{19}F_{eq}-^{119}Sn  = 1744$
	$F_{ax}$	-165.28 (tr) (2)	$^2J^{19}F_{eq}-^{19}F_{ax} = 36.8$ ; $ ^1J^{19}F_{ax}-^{117}Sn  = 1406$ ; $ ^1J^{19}F_{ax}-^{119}Sn  = 1468$
	$F_{br}$	-147.0 (s) (1)	$ ^1J^{19}F_{br}-^{117/119}Sn  = 1196$
	$Sn^\square$	-865.6 (tr,tr,tr)	$ ^1J^{19}F_{eq}-^{119}Sn  = 1740$ ; $ ^1J^{19}F_{ax}-^{119}Sn  = 1440$ ; $ ^1J^{19}F_{br}-^{119}Sn  = 1200$
$Sn_4F_{20}^{4-}$	$F_{eq}$	-174.2 (tr) (2)	$^2J^{19}F_{eq}-^{19}F_{ax} = 36.3$ ; $ ^1J^{19}F_{eq}-^{117}Sn  = 1622$ ; $ ^1J^{19}F_{eq}-^{119}Sn  = 1697$
	$F_{ax}$	-165.33 (tr) (2)	$^2J^{19}F_{eq}-^{19}F_{ax} = 36$ ; $ ^1J^{19}F_{ax}-^{117/119}Sn  = 1440$
	$F_{br}$	-145.0 (s) (1)	$ ^1J^{19}F_{br}-^{117}Sn  = 1178$ ; $ ^1J^{19}F_{br}-^{119}Sn  = 1230$
	$Sn^\square$	-865.2 (tr,tr,tr)	$ ^1J^{19}F_{eq}-^{119}Sn  = 1760$ ; $ ^1J^{19}F_{ax}-^{119}Sn  = 1468$ ; $ ^1J^{19}F_{br}-^{119}Sn  = 1230$

<sup>a</sup> Coupling constants derived from simulated spectra

Table 4. Raman and Infrared spectra\* of solid  $N_5B(CF_3)_4$  and their assignments

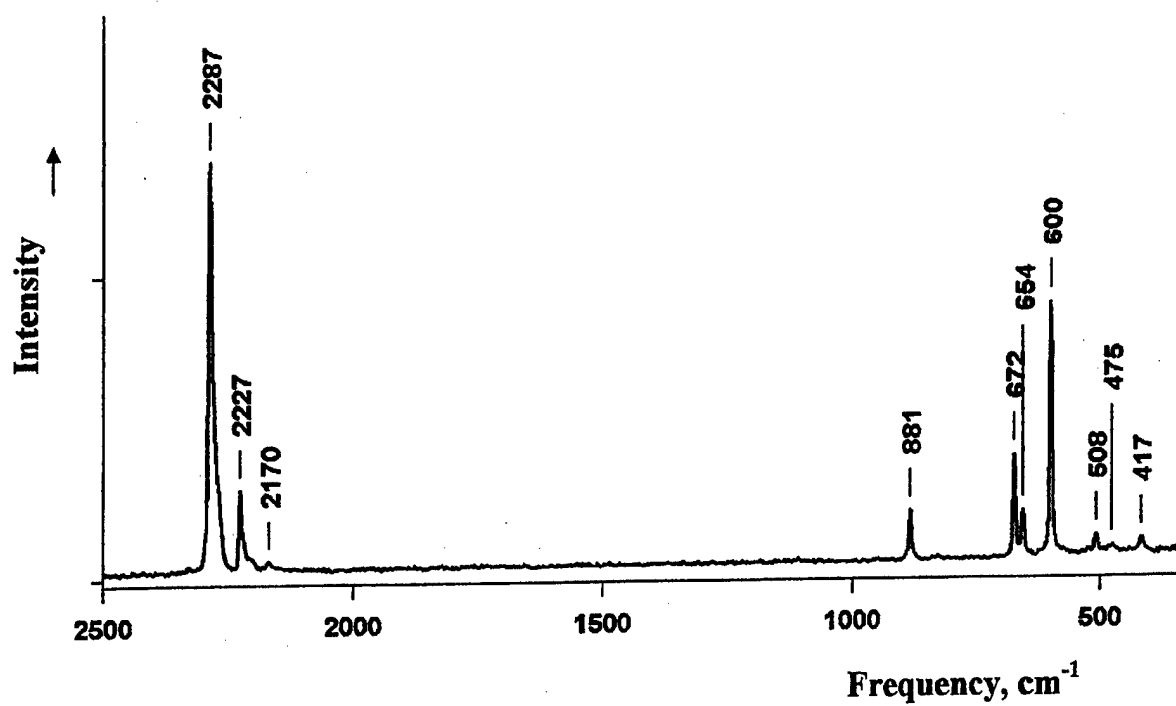
Obsd frequencies, $cm^{-1}$ , and rel intens		Assignments (point group)	
Raman	Infrared	$N_5^+ (C_{2v})$	$B(CF_3)_4^- (T)$
	3307 w	$(\nu_1 + \nu_8)(B_2) = 3316$	
	3057 w	$(\nu_2 + \nu_7)(B_2) = 3060$	
	2662 w	$(\nu_1 + \nu_9)(B_2) = 2663$	
	2375 w		$(\nu_9 + \nu_{10})(F) = 2376$
2257 (10.0)	2256 m	$\nu_1(A_1)$	
2200 (2.7)	2197 ms	$\nu_7(B_2)$	
1290 (sh)	1292 sh		$\nu_9(F)^{10}B$
1276 (1.6)			$\nu_1(A)$
1270 (sh)	1273 vs		$\nu_9(F)^{11}B$
1103 (0.6)(br)	1115 vs, br		$\nu_{10}(F)$
1086 (sh)			$\nu_5(E)$
	1060 sh	$\nu_8(B_2)$	
	929 s		$\nu_{12}(F)^{10}B$
	902 vs		$\nu_{12}(F)^{11}B$
863 (0.6)		$\nu_2(A_1)$	
728 (6.2)			$\nu_2(A)$
	696 s		$\nu_{13}(F)$
672 (sh)		$\nu_3(A_1)$	
525 (1.8)	521 ms		$\nu_{14}(F)$
525 (1.8)	521 ms		$\nu_{15}(F)$
	489 m	$\nu_5(A_2)$	
	443 w		
	419 m	$\nu_6(B_1)$	
	407 sh	$\nu_9(B_2)$	
319 (2.1)			$\nu_7(E)$
295 (3.3)			$\nu_{16}(F)$
279 (2.7)			$\nu_3(A)$
209 (3.4)		$\nu_4(A_1)$	
110 (0.5)(sh)			$\nu_8(E)$

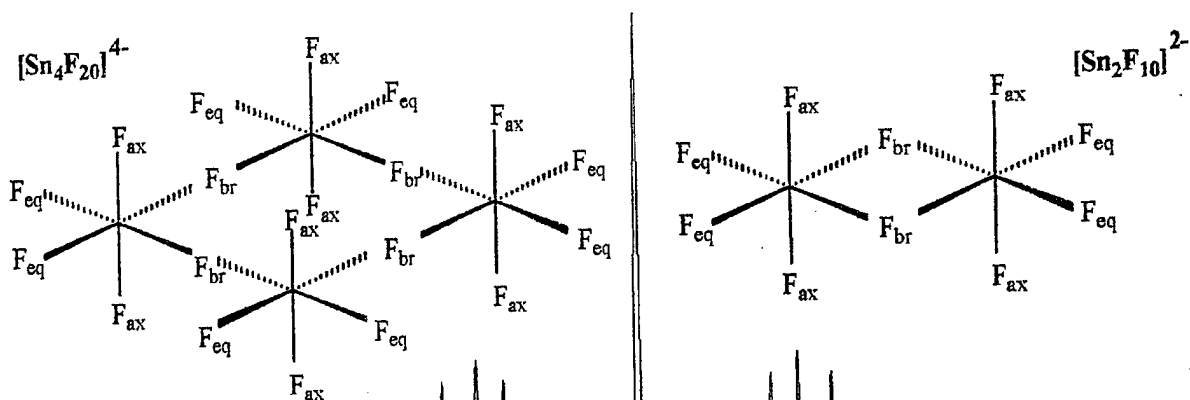
\*The following bands due to the  $SbF_6^-$  impurity were also observed. Ra: 659 (7.0),  $\nu_1$ ; 574 (0.7),  $\nu_2$ ; 295 (3.3) and 279 (2.7),  $\nu_5$ ; IR: 664 s, br,  $\nu_3$ .

### Figure Captions

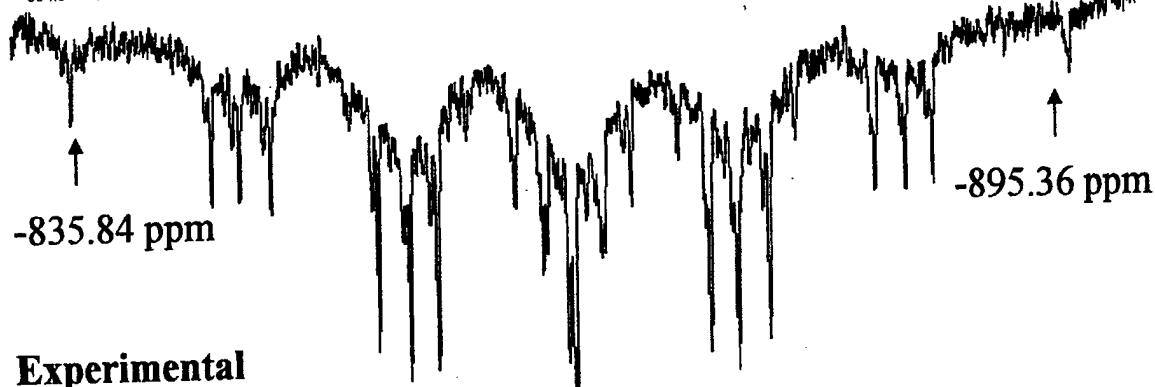
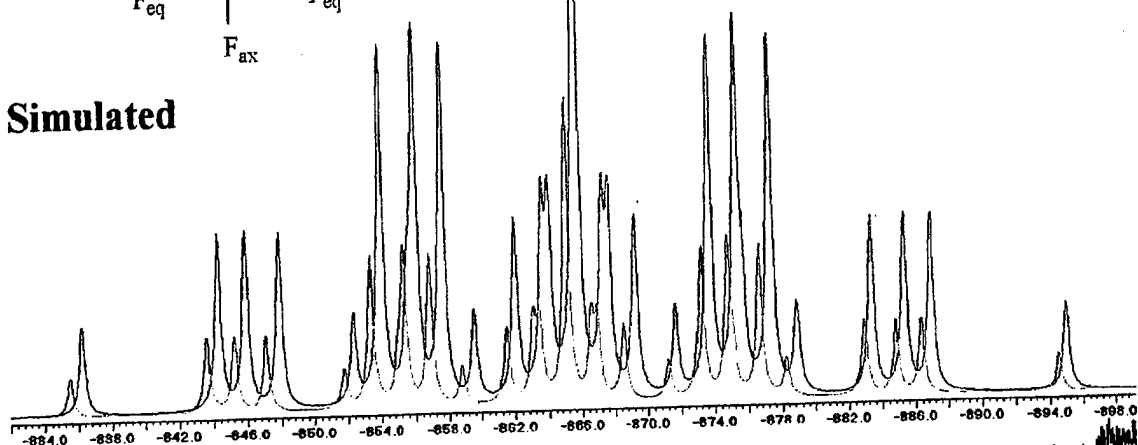
Figure 1. Raman spectrum of solid  $(N_5)_2SnF_6$ .

Figure 2. Observed (black trace) and simulated  $^{119}Sn$  NMR spectra of  $Sn_2F_{10}^{2-}$  (red trace) and  $Sn_4F_{20}^{4-}$  (blue trace) in a 2 : 1 mole ratio.





**Simulated**

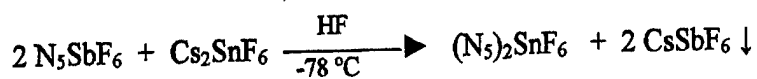


**Experimental**

BEST AVAILABLE COPY

## Synopsis

The successful synthesis of the 2:1 salt  $(N_5^+)_2SnF_6^{2-}$  demonstrates that compounds with touching polynitrogen cations can be prepared, and that the synthesis of an ionic, all nitrogen compound is in principal possible. This paper also shows that  $N_5^+$  salts, other than  $N_5SbF_6$  and  $N_5AsF_6$ , can be prepared by metathetical reactions. This method was applied to the syntheses of  $N_5B(CF_3)_4$ ,  $N_5^+SnF_5^-$ , and  $(N_5^+)_2SnF_6^{2-}$ .



W. W. Wilson,\* A. Vij, V. Vij,  
E. Bernhardt, K. O. Christe\*

Polynitrogen Chemistry. Preparation and Characterization of  $(N_5)_2SnF_6$ ,  $N_5SnF_5$ , and  $N_5B(CF_3)_4$

**Keywords:** fluorostannate anions · NMR spectroscopy · pentanitrogen(+1) cation · polynitrogen · tetrakis(trifluoromethyl)borate anion · vibrational spectroscopy

BEST AVAILABLE COPY